

# High Density Polyethylene/Acrylonitrile Butadiene Rubber Blends: Morphology, Mechanical Properties, and Compatibilization

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## SYNOPSIS

Polymer blends based on high-density polyethylene (HDPE) and acrylonitrile butadiene rubber (NBR) were prepared by a melt blending technique. The mixing parameters such as temperature, time, and speed of mixing were varied to obtain a wide range of properties. The mixing parameters were optimized by evaluating the mechanical properties of the blend over a wide range of mixing conditions. The morphology of the blend indicated a two-phase structure in which NBR phase was dispersed as domains up to 50% of its concentration in the continuous HDPE matrix. However, 70 : 30 NBR/HDPE showed a co-continuous morphology. The tensile strength, elongation at break, and hardness of the system were measured as a function of blend composition. As the polymer pair is incompatible, technological compatibilization was sought by the addition of maleic-modified polyethylene (MAPE) and phenolic-modified polyethylene (PhPE). The interfacial activity of MAPE and PhPE was studied as a function of compatibilizer concentration by following the morphology of the blend using scanning electron micrographs. Domain size of the dispersed phase showed a sharp decrease by the addition of small amounts of compatibilizers followed by a leveling off at higher concentrations. Also, more uniformity in the distribution of the dispersed phase was observed in compatibilized systems. The tensile strength of the compatibilized systems showed improvement. The mechanical property improvement, and finer and uniform morphology, of compatibilized systems were correlated with the improved interfacial condition of the compatibilized blends. The experimental results were compared with the current theories of Noolandi and Hong. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Polymer blending is one of the new approaches for the preparation of new materials from existing polymers. One obvious advantage is that it requires little or no capital expenditure relative to the production of new polymers. Also, it is possible to produce a range of materials with properties completely different from those of the blend constituents.

It is generally considered that polymers are not thermodynamically compatible (miscible). In order

to be thermodynamically miscible, the Gibb's free energy of mixing ( $\Delta G_m$ ) must be negative or zero in the expression,

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

where  $\Delta H_m$  and  $\Delta S_m$  represent the enthalpy and entropy of mixing, respectively.  $H_m$  is essentially independent of molecular weight and is a measure of the energy changes associated with intermolecular interaction, whereas the entropy change is essentially an inverse function of molecular weight. Because of the long chain nature of polymer molecules, the number of possible arrangements upon mixing

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becomes less, which means that there is little negative contribution to the free energy of mixing.

Most of the blends used in structural applications consist of two or more phases. This arises because the inclusion of rubbery particles within a glassy matrix can produce an improvement in impact and other properties without too large a decrease in modulus. Miscible polymers are used as polymeric plasticizers when a decrease in modulus is desired, and these find application in PVC blends.<sup>1</sup> One can also make homogeneous blends of two glassy polymers having different glass transition temperatures in order to have a wide range of processability and a corresponding range of high-temperature use properties.

Polymer blends can be prepared by a variety of techniques, which include solution blending, latex blending, mechanical blending, and mechanochemical blending. The various preparation techniques have been extensively reviewed in the literature.<sup>2,3</sup> Each method has its own merits and demerits. Even though melt mixing is the most widely used commercial technique, it also has some problems. Because of the large size of polymer molecules, they don't easily mix. Also, there is the chance of degradation at high temperatures. Moreover, in some cases, phase separation may occur at high temperatures.

It is an obvious advantage that, for many applications, complete miscibility is not required. Commercial importance can be achieved for immiscible systems that are technologically compatibilized. In such cases, the advantage is that the resultant blend properties are synergistic and the morphology of the minor phase in the matrix polymer is finer and homogeneous.

There are different ways to achieve such compatibilization, the most common of which is the introduction of a suitably chosen block or graft copolymer.<sup>4-8</sup> The segments of these copolymers can be chemically identical with those in the respective phases<sup>6-10</sup> or miscible with or adhered to one of the phases.<sup>11-13</sup> The interfacial activity of block and graft copolymers has been reviewed by Paul.<sup>14</sup> The morphological observations of Molau et al.<sup>15-17</sup> clearly demonstrate the ability of block copolymers to emulsify polymer dispersions in solutions and, thus, to inhibit phase separation.

Thermoplastic elastomers based on rubber/plastic blends are important branches of polymer blend systems. The advantages of such systems are the excellent processing characteristics of thermoplastic materials at a high temperature and the rubbery be-

havior at a service temperature.<sup>18-22</sup> Among the different types of thermoplastic elastomers, those prepared by physical blending of an elastomer and a thermoplastic material under high shearing action have gained considerable attention due to the simpler method of preparation and easy attainment of the desired physical properties.<sup>23</sup> During the last 2 decades, a considerable amount of work has been reported on thermoplastic elastomer blends. Properties of EPDM-PP thermoplastic blends with partial cross-linking of the elastomer phase were reported by Fisher.<sup>24</sup> Campbell, Elliott, and Wheelans<sup>25</sup> have described the method of preparation, injection molding conditions, and physical properties of NR-PE and NR-PP blends. Rheology, morphology, mechanical properties, and failure mode of various thermoplastic elastomer blends have been reported by De and co-workers.<sup>26-32</sup> Coran and Patel<sup>33-38</sup> have published a series of articles on rubber/thermoplastic blends. They have reported compositions containing a particular thermoplastic and vulcanized rubber particles. Also, they have functionalized<sup>39,40</sup> the polymers to enhance overall mechanical properties.

In the present study, thermoplastic elastomers based on high-density polyethylene (HDPE) and nitrile rubber (NBR) were prepared by a melt-blending technique. These blends couple the elastic and oil-resistance properties of NBR and the excellent mechanical properties, ozone resistance, and processability characteristics of HDPE. Because the system is incompatible, technological compatibilization was sought by the addition of maleic- and phenolic-modified polyethylene. The compatibilizer locates at the interface and reduces the interfacial tension and, thus, provides improved adhesion between the phases. The influence of the compatibilizer on the morphology and properties of the blends has been quantitatively analyzed. The experimental results were applied to test the current compatibilization theories of Noolandi and Hong.

## EXPERIMENTAL

### Materials

High-density polyethylene (HDPE, Indothene HD 58 MA 075) of density 0.958 g/cc and melt flow index value of 7.5 g/10 min was obtained from the Indian Petrochemicals Corporation Ltd., Baroda. Acrylonitrile butadiene rubber (NBR) was received from M/s. Synthetics and Chemicals, Bareilly, U.P.

The acrylonitrile content and density of the material were 32% and 0.98 g/cc, respectively. Phenolic-modified polyethylene (PhPE) was prepared by melt blending HDPE (100 g) with dimethylol phenolic resin (4 g) and stannous chloride (0.8 g), and maleic-modified polyethylene (MAPE) was prepared by melt mixing HDPE (100 g) with maleic anhydride (5 g) and dicumyl peroxide (0.5 g).<sup>38-40</sup> The melt mixing was carried out in a Brabender Plasticorder at 180°C and 60 rpm. The modified materials were removed from the mixer and cut into small pieces for use as compatibilizers.

The blends were designated as H<sub>100</sub>, H<sub>70</sub>, H<sub>50</sub>, H<sub>30</sub>, and H<sub>0</sub>, where the subscripts indicate the amount of HDPE in the blend. In the modified systems, 'M' stands for maleic-modified polyethylene and 'P' stands for phenolic-modified PE. The subscripts following 'M' and 'P' indicate the amount of the modified PE added into the blend. For example, H<sub>70</sub>M<sub>1</sub> indicates a blend of 70 HDPE/30 NBR containing 1% maleic modified polyethylene.

### Blending and Molding

Melt mixing was carried out in a Brabender Plasticorder (PLE 331) having a capacity of 65 cc. For the optimization of mixing parameters, blending was carried out over a temperature range from 150 to 180°C, mixing time from 6 to 15 min, and rotor speeds from 40 to 70 rpm. In order to optimize each parameter, that parameter was varied over a range while maintaining the other two parameters constant. For the blend preparation, the HDPE was melted for 2 min and then the rubber was added. The mixing was continued for 6 min. For the compatibilized systems, after melting HDPE for 2 min, the modifier was added and mixed for 2 min, followed by the addition of rubber. The mixing time was noted after the complete transfer of all the materials into the mixing chamber. Test samples were prepared by compression molding in a hydraulic press at the respective blending temperatures.

### Testing Procedure

Tensile testing of the samples was done according to ASTM D412-80 test method using dumbbell samples at a crosshead speed of 500 mm/min using a Zwick Universal Testing Machine (model 1474).

Hardness was measured according to the ASTM D2240-81 test method using a shore A durometer. For hardness measurement, sufficient numbers of sheets were placed one over another to get a thick-

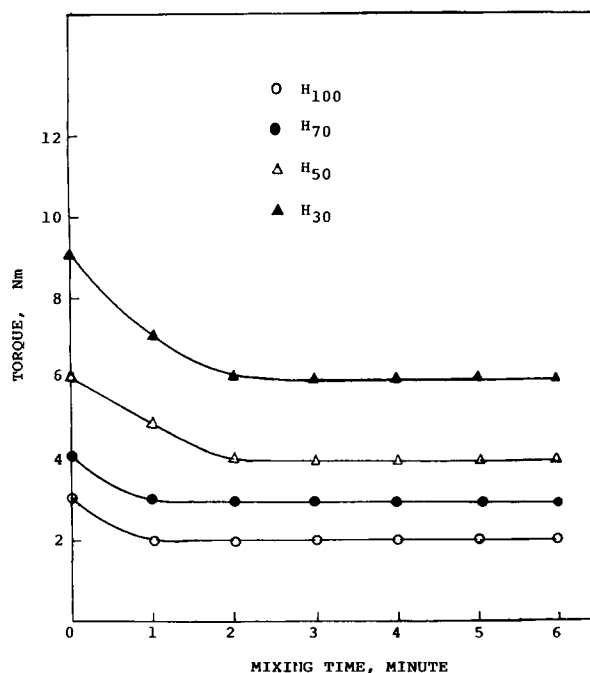
ness of at least 6 mm, taking care that the surfaces of the sheets were flat.

The blend morphology was studied by using a Scanning Electron Microscope (JEOL JSM 35C) after sputter coating the samples with gold on a FINE COAT ion Sputter (JEOL JSM 1100). The surface analysis was studied by using cryogenically fractured samples. In order to facilitate identification of the phase and to enhance morphological features, the NBR phase was preferentially extracted using chloroform. The crystallinity of pure HDPE and the blends were evaluated from the differential scanning calorimetry studies using a Perkin-Elmer thermal analyser. The heating rate was 20°C/min.

## RESULTS AND DISCUSSION

### Optimization of Mixing Parameters

The variation of the mixing torque and the stock temperature, developed with time of mixing at the optimum mixing conditions, are shown in Figures 1 and 2, respectively. As evident from Figure 1, in all cases the torque decreases with mixing time and levels off at 3 min of mixing. The leveling off of the torque may be related to the leveling of the time-temperature profile (Fig. 2) as well as to the attain-



**Figure 1** Variation of mixing torque as a function of mixing time of HDPE/NBR blends.

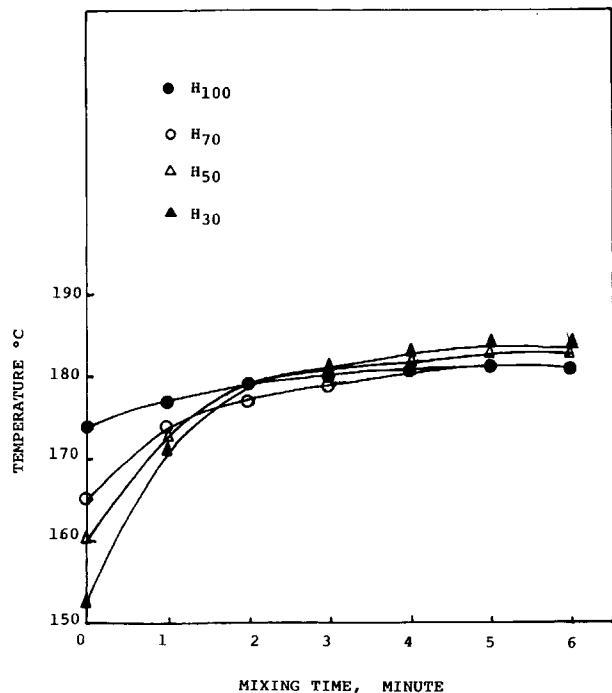


Figure 2 Change in mixing temperature with mixing time of HDPE/NBR blends.

ment of a good level of mixing. The initial and final torques of the blends increase with increase of NBR content. This is attributed to the high viscosity of NBR as compared to HDPE.

The progress of the stock temperature as a function of mixing time is given in Figure 2. The mixing chamber was maintained at 180°C before the introduction of the materials. The initial lowering of stock temperature is due to the addition of NBR into molten HDPE. The temperature shows a steep rise initially and then a leveling off within 3 min of mixing. Even though a leveling off in torque and temperature was observed after 3 min, we have selected 6 min for a good level of mixing as the number of ingredients are more in compatibilized systems. Also, it is clear from Figures 1 and 2 that there is no reduction in torque or increase in temperature on continued mixing up to 6 min. This indicates that there is no degradation taking place. Hence, the selection of 6 min is quite justifiable.

The effect of mixing parameters such as mixing temperature, time of mixing, and speed of mixing on tensile strength and elongation at break of H<sub>70</sub> blend is given in Figures 3, 4, and 5, respectively. In order to study the effects of each parameter, the other two parameters are maintained constant.

In Figure 3, the effect of temperature is studied by varying it from 150–180°C while the mixing speed

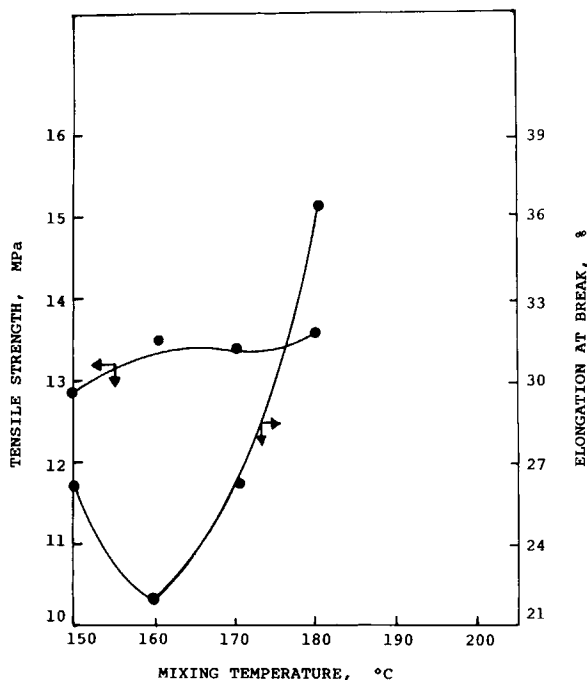


Figure 3 Variation of tensile strength and elongation at break of H<sub>70</sub> as a function of mixing temperature.

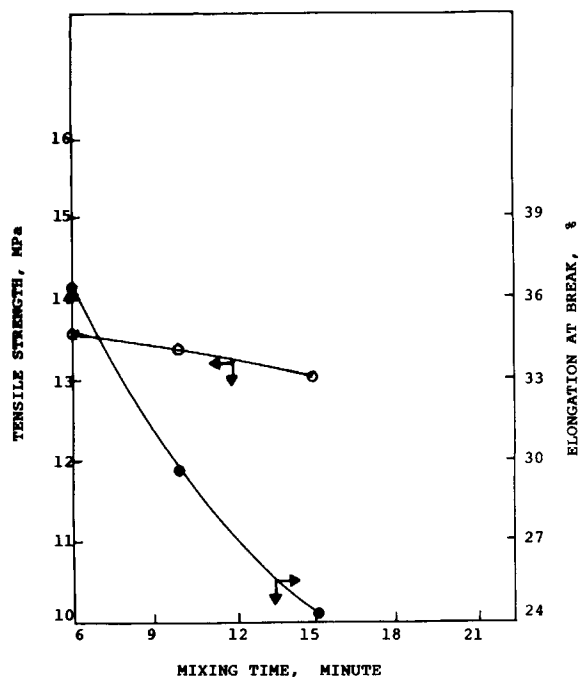
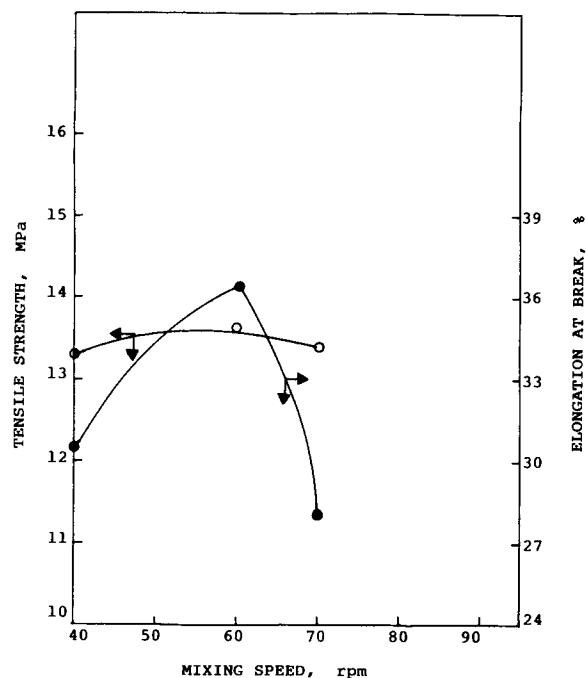


Figure 4 Variation of tensile strength and elongation at break of H<sub>70</sub> with time of mixing.



**Figure 5** Effect of mixing speed on the tensile strength and elongation at break of H<sub>70</sub>.

and time are maintained constant at 60 rpm and 6 min, respectively. As evident from the figure, there is a gradual increase in tensile strength as the mixing temperature is increased from 150 to 180°C. But the elongation at break shows a decrease at 160°C and

then an increase as the mixing temperature is increased. At a high temperature, there occurs a good level of mixing between the crystalline HDPE and NBR as the NBR domains are broken down into smaller ones.

In order to study the effect of mixing time on properties, the mixing temperature and rotor speed are maintained constant at 180°C and 60 rpm, respectively, while the time of mixing is varied from 6 to 15 min. As seen from Figure 4, there is a gradual decrease in tensile strength and a sharp decrease in elongation at break as the mixing time is increased. This may be due to the degradation of the blend system as the mixing time is prolonged.

The variation of tensile strength and elongation at break as a function of mixing speed are given in Figure 5. Here, the mixing speed is varied from 40 to 70 rpm while the temperature and time of mixing are maintained at 180°C and 6 min, respectively. Even though the tensile strength is not affected much by the speed of mixing, there is a marked reduction in elongation at break at 70 rpm. In fact, at a higher speed, more particle break down and an enhancement in properties was expected. However, the observed reduction in tensile strength and elongation at break at 70 rpm may be due to the fact that at a high temperature, on increasing the mixing speed, the viscosity of HDPE will come down fast and, because of this viscosity mismatch between HDPE and NBR, effective shearing may not be pos-

**Table I** Effect of Processing Parameters on Modulus at 15% Elongation of H<sub>70</sub>.

Parameters Kept Constant	Parameters Varied	Modulus at 15% Elongation (MPa)
Rotor speed 60 rpm and time 6 min	<u>Temperature (°C)</u>	
	150	12.5
	160	13.1
	170	12.9
Temperature 180°C and time 6 min	<u>Rotor speed (rpm)</u>	
	40	12.5
	60	13.3
	70	12.9
Temperature 180°C and rotor speed 60 rpm	<u>Time (min)</u>	
	6	13.3
	10	12.7
	15	12.55

sible. This leads to poor intermixing, which results in a reduction in properties.

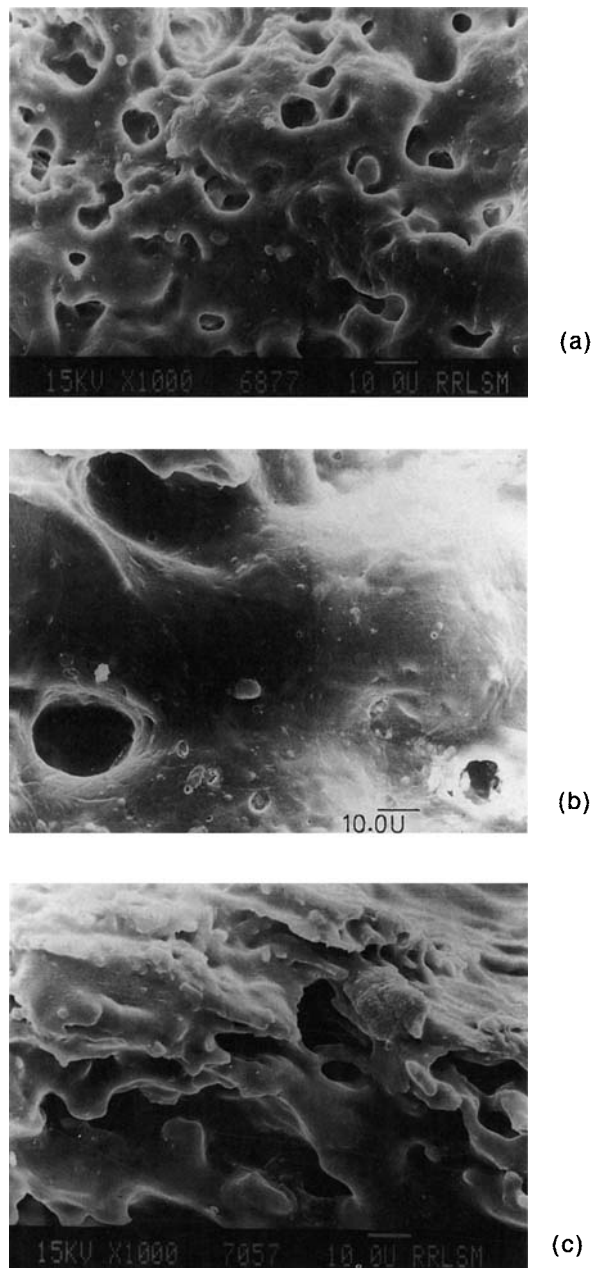
The modulus at 15% elongation of  $H_{70}$  as a function of processing parameters is shown in Table I. The modulus shows a similar trend as tensile strength. Although the modulus values are very close, a maximum is obtained at 180°C, 60 rpm and 6 min mixing.

Based on the tensile strength, elongation at break, and modulus data, it can be concluded that for the best balance of properties, HDPE/NBR blending in a Brabender Plasticorder should be carried out at a temperature of 180°C for a period of 6 min and at a rotor speed of 60 rpm.

### Effect of Blend Ratio on Morphology and Mechanical Properties

Morphology is a major determinant of the properties of heterogeneous polymer blends. The main physical factors that determine the final morphology of the blends are component ratio, their intrinsic melt viscosity, rate of shear during melt mixing, and the presence of other ingredients. Nielsen<sup>41</sup> has shown that the phase morphology of polyblends, prepared by melt mixing, changes as a function of composition. Callan et al.<sup>42</sup> have extensively studied the composition dependence of morphology of polymer blends. Paul and Barlow<sup>43</sup> and Han<sup>44</sup> have shown that the morphology created during mixing depends on interfacial tension between the phases and the viscosity and elasticity. The size of the dispersed phase is further determined by the drop break up<sup>45</sup> and coalescence<sup>46</sup> phenomena. The morphology can also be affected by the conditions of mixing. Avgeropoulos et al.<sup>47</sup> have shown that for a 50 : 50 EPDM/BR blend the phase morphology is highly dependent on mixing temperature. The work of Avgeropoulos et al.<sup>47</sup> and Hamed<sup>48</sup> have clearly shown the effect of mixing time on the morphology of melt-mixed elastomer blends. The dispersed phase size is also affected by the mixing torque and mixing torque mismatch. As reported by Avgeropoulos,<sup>47</sup> when the mixing torques are well matched and when they are high, then the smallest domain sizes are obtained. Although these studies deal with rubber-rubber blends, similar results have been obtained for rubber-plastic blends. Danesi and Porter<sup>49</sup> have shown that, for the same processing history, the composition ratios and melt viscosity differences of the components determine the morphology. When the mixed polymers have similar melt viscosities, the resultant morphology indicates a uniform distribu-

tion of the minor component in the major one, no matter which is the minor component. When the components have different melt viscosities, the morphology of the resultant blend depends on whether the minor component has a lower viscosity or higher viscosity than the major one. If the minor component has a lower viscosity, this component

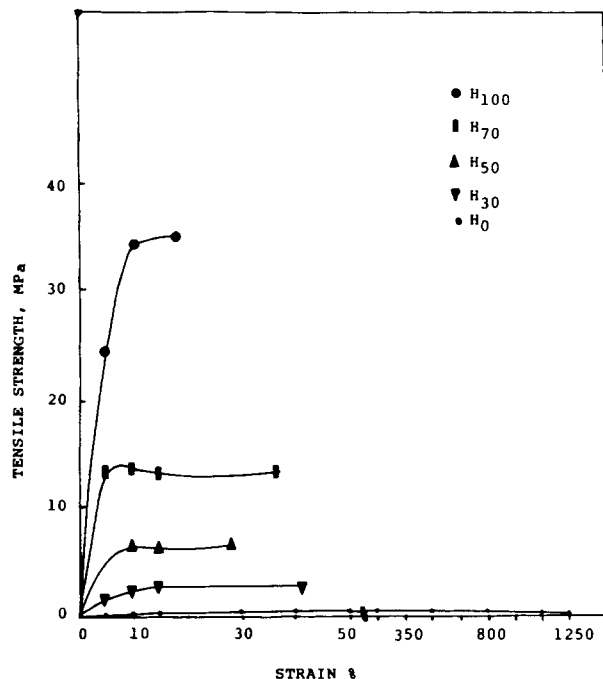


**Figure 6** (a) SEM photomicrograph of  $H_{70}$  showing dispersed domains of NBR. (b) SEM photomicrograph of  $H_{50}$  showing dispersed rubber particles. (c) SEM photomicrograph showing cocontinuous morphology for  $H_{30}$ .

will be finely dispersed. In contrast, the minor component will be coarsely dispersed in essentially spherical domains if its viscosity is higher than that of the major one.

The scanning electron micrographs of the blends  $H_{70}$ ,  $H_{50}$ , and  $H_{30}$ , from which NBR phase has been extracted by chloroform, are shown in Figure 6(a) to (c). In this figure, the holes indicate the rubber phase that has been extracted. From figure 6(a) and (b), it is clear that the rubber phase remained as dispersed particles in the continuous HDPE matrix in blends  $H_{70}$  and  $H_{50}$ . The domain size of the dispersed phase in  $H_{70}$  and  $H_{50}$  are  $7.15 \mu\text{m}$  and  $19.38 \mu\text{m}$ , respectively. The increase in domain size with increasing concentration of NBR is due to the phenomenon of agglomeration or coalescence. Occurrence of coalescence at higher concentrations of one of the components has been reported by many authors.<sup>50-54</sup> Heikens and Barentsen<sup>53</sup> have observed that in polyethylene/polystyrene blends, the increase in particle dimension of PE at higher concentrations is caused by coalescence. Particle recombination (or coalescence) has been reported at higher concentrations of Hytrel<sup>™</sup> in PVC/Hytrel blends by Thomas et al.<sup>54</sup> The dispersed nature of NBR in  $H_{50}$  and  $H_{70}$  is associated with its higher viscosity as compared to HDPE. The viscosity effects may be offset by the proportion of the components. Thus, at higher proportions of NBR, a co-continuous morphology is obtained [Fig. 6(c)], where HDPE and NBR form the continuous phases.

Figure 7 shows the stress-strain behavior of the samples. The difference in the deformation characteristics of the blends under an applied load are evident from this figure. HDPE shows the highest tensile strength. From the stress-strain behavior of HDPE it is clear that it shows a yielding tendency typical of tough plastics. The addition of nitrile rubber considerably changes the stress-strain behavior. The moduli of the samples are considerably reduced by the addition of nitrile rubber. In general, the stress-strain curves of samples containing a higher amount of HDPE ( $\geq 50\%$ ) have elastic and inelastic regions. In the inelastic region, the samples undergo yielding and/or necking. The strength of HDPE/NBR blends depends on the HDPE matrix, which in turn, is determined by the extent of crystallinity. Martuscelli et al.<sup>55</sup> have shown that the spherulitic growth of isotactic polypropylene in blends with rubber is hindered by the presence of soft rubber. Also, in these sorts of crystalline/amorphous incompatible blends premature failure may occur due to the presence of overly large rubber particles,

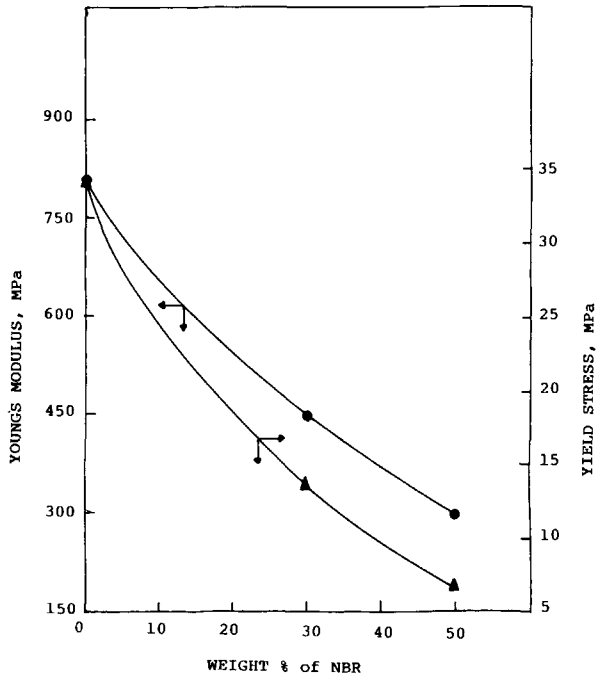


**Figure 7** Tensile stress-strain curves of HDPE/NBR blends as a function of blend ratio.

which act as failure initiating flaws. It has been reported that the strength of a rubber/plastic blend can be greatly reduced if the dispersed rubber particles are large enough, even when the interfacial adhesion is good.<sup>33,56</sup> In  $H_{70}$  and  $H_{50}$  we can see yielding and necking behavior. On further increasing the rubber content, the necking tendency characteristic of plastics disappears and rubbery behavior is exhibited by  $H_{30}$ . The stress-strain curve of NBR is typical of the stress-strain curve of low modulus rubbery material.

The phase-change morphology can be inferred from stress-strain curves. The blends exhibit typical plastic behavior up to 50% HDPE. This indicates that, up to 50% HDPE, the NBR is dispersed in a continuous HDPE matrix. On further increasing the rubber content, the necking tendency disappears. From the disappearance of necking and from the sharp reduction in tensile strength for  $H_{30}$ , we can conclude that in this system both NBR and HDPE are forming continuous phases, which is also evident from the scanning electron micrograph [Fig. 6(c)].

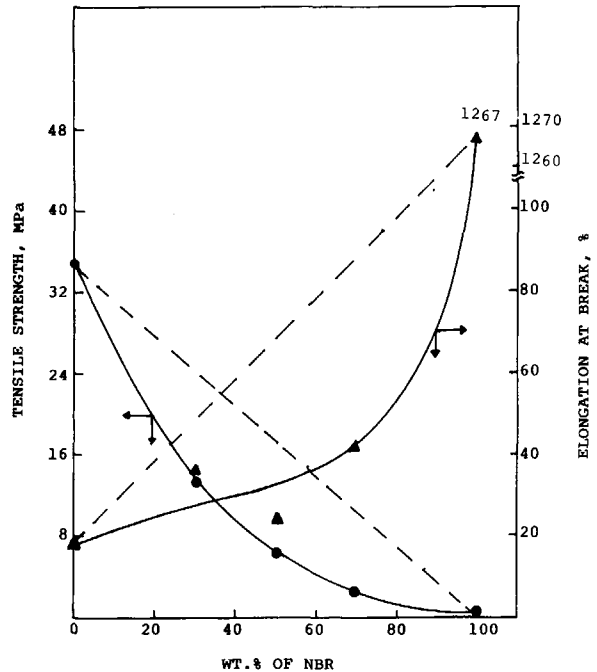
The Young's modulus and yield stress of HDPE/NBR blends as a function of blend ratio are given in Figure 8. Pure HDPE has a Young's modulus of  $\approx 812 \text{ MPa}$ . On adding NBR, there is a drastic reduction in the Young's modulus values. This is due to the fact that NBR is a very low modulus material



**Figure 8** Variation of Young's modulus and yield stress with NBR content.

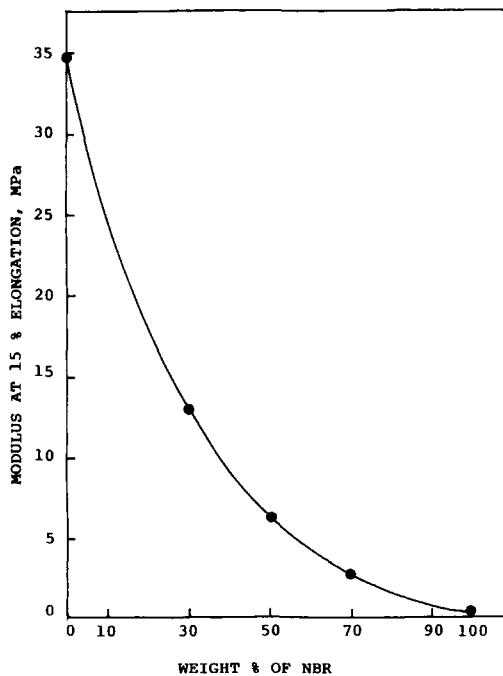
and also to the reduced crystallinity of the blend. From the differential scanning calorimetry data it was found that the crystallinity of H<sub>100</sub>, H<sub>70</sub>, H<sub>50</sub>, and H<sub>30</sub> were 65, 45, 33, and 16.5%, respectively. The explanation given for the reduction in Young's modulus values of the blend with the addition of rubber also explains the reduction in yield stress values upon the addition of rubber.

Figure 9 shows the effect of blend ratio on tensile strength and elongation at break of HDPE/NBR blends. As is evident from the figure, HDPE is a highly crystalline material having very good tensile strength, while NBR is an amorphous material having very poor tensile strength. As expected by the addition of NBR, the tensile strength decreases. The reduction in crystallinity of isotactic polypropylene on the addition of rubber has been reported by Martuscelli et al.<sup>55</sup> In this case, the reduction in tensile strength on the addition of rubber may be due to the reduced crystallinity of the blend compared to pure HDPE. Usually, the blend properties are determined by the nature of the components and the thermodynamic state of the blend. In an immiscible blend, properties related to ductility are related not only to those of the separate phases but also to the domain size and the degree of adhesion between the phases. As seen from the figure, the blends H<sub>70</sub>, H<sub>50</sub>, and H<sub>30</sub> show much lower tensile strength than pro-



**Figure 9** Effect of blend ratio on tensile strength and elongation at break of HDPE/NBR blends.

jected from the additive level. The observed negative deviation is associated with the reduced crystallinity and poor interfacial adhesion between the phases.



**Figure 10** Variation of modulus at 15% elongation as a function of NBR content for HDPE/NBR blends.



As seen from Figure 9, NBR has a very high elongation at break, while HDPE has a very low value. The blends have intermediate values but, again, are much lower than projected from the additive level. This is due to the incompatibility and poor adhesion between phases. From the figure it is clear that there is no slope change up to 60% NBR content. Further increase in proportion of the rubber phase causes an abrupt increase in the elongation at break. This is associated with the fully continuous nature of the rubber phase.

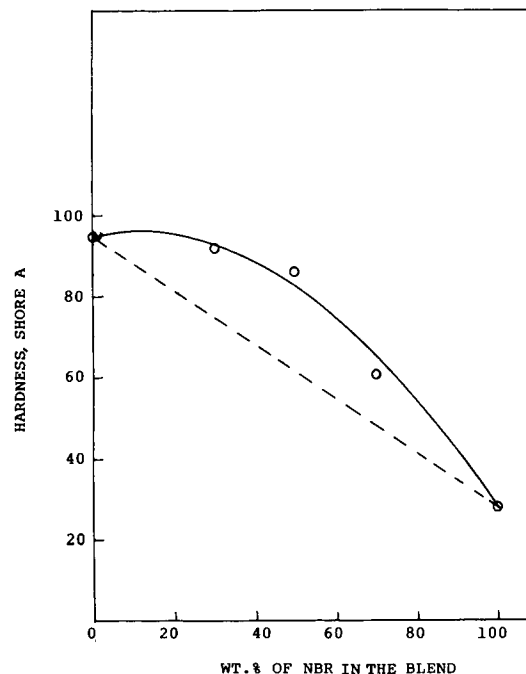
Figure 10 shows the effect of blend ratio on the modulus at 15% elongation of HDPE/NBR blends. Pure HDPE has a very high modulus, which decreases sharply on the addition of NBR. The reduction in modulus values on the addition of NBR is due to the low modulus of NBR and also due to the reduced crystallinity of the blend containing increased proportions of rubber. The tensile strength and modulus data show similar trends.

One of the important advantages of thermoplastic elastomers is that they exhibit a wide range of hardness. In Figure 11, the Shore A hardness as a function of blend composition is given. The hardness values range from 95 to 28 Shore A. Pure HDPE shows the highest value of Shore A hardness, while NBR shows the lowest. As expected, the blends have decreasing hardness values as the NBR content increases. The hardness values lie above the additivity line because it is a surface property and is much less related to the interfacial bonding.

### Compatibilization

Frequently, two polymers are thermodynamically immiscible. This may not be a problem always because it is often desirable to have a two-phase structure. However, the interface between these two phases often leads to problems. High interfacial tension and poor adhesion between the two phases can lead to severe service limitations in a blend. The high interfacial tension can lead to improper dispersion, domains with large dimensions, and lack of stability against coalescence and gross separation during later processing or use. Poor adhesion leads to very weak and brittle mechanical behavior.<sup>4</sup> These problems can be overcome by the use of compatibilizers. Thus, a compatibilizer improves the interfacial condition of an immiscible blend.

Usually, a third component, block, or graft copolymer is used as a compatibilizer.<sup>7,10,57</sup> The general view is that a properly chosen third component should preferentially locate at the interface between



**Figure 11** Shore A hardness as a function of NBR content of HDPE/NBR blends.

the two phases. An ideal compatibilizer should be a material that can interact with both the phases. This type of surface activity reduces the interfacial tension between the phases, permits a finer dispersion during mixing, provides a measure of stability against gross segregation, and results in improved interfacial adhesion.<sup>58</sup>

As seen earlier, HDPE/NBR blends are immiscible, showing poor mechanical properties. This immiscibility is due to the disparity in polarity between the two homopolymers. As a result of the very poor physical and chemical interaction across the phase boundaries, the mechanical properties of HDPE/NBR blends are below the additivity line. This problem can be overcome by the use of compatibilizers.

Grafting of preformed polymers is an important method for the preparation of polymers with functional groups. Maleic anhydride (MAN) is a reactive monomer, and it has been grafted to PE by mechanical, free radical, ionic, and radiation techniques.<sup>59,60</sup> The grafting process may be carried out in solution, in molten PE, or on suspended films. The pendant anhydride group provides functionality for crosslinking and other chemical reactions, and it aids compatibility of PE with other polymers.

Several reports are available on the grafting of MAN on to PE<sup>61-63</sup> in the presence of peroxide. Gay-

lord et al.<sup>64</sup> reported that the heterogeneous reaction of MAN with molten PE in the presence of benzoyl peroxide at 140° and at 180°C resulted in the grafting of both poly(MAN) chains and single MAN units to the PE. Gaylord and Mehta<sup>65</sup> showed that the presence of MAN in a PE-cumyl peroxide mixture at 180°C also leads to increased crosslinking but can be reduced or eliminated by the addition of various nitrogen-, phosphorous-, and sulfur-containing organic electron donors.

Coran and Patel<sup>39,40</sup> have functionalized polyolefin with dimethylol phenolic resin (SP-1045), which can

be used to enhance the compatibility of polyolefins with other polymers. This reaction requires the presence of olefinic unsaturation in the polyolefin molecule.

In the present system, maleic-modified polyethylene (MAPE) and phenolic-modified polyethylene (PhPE) are used as compatibilizers to improve the interfacial condition of the incompatible HDPE/NBR blends.

### Mechanism of Grafting

The well-known peroxide mechanism explains the grafting and/or crosslinking reaction when PE is

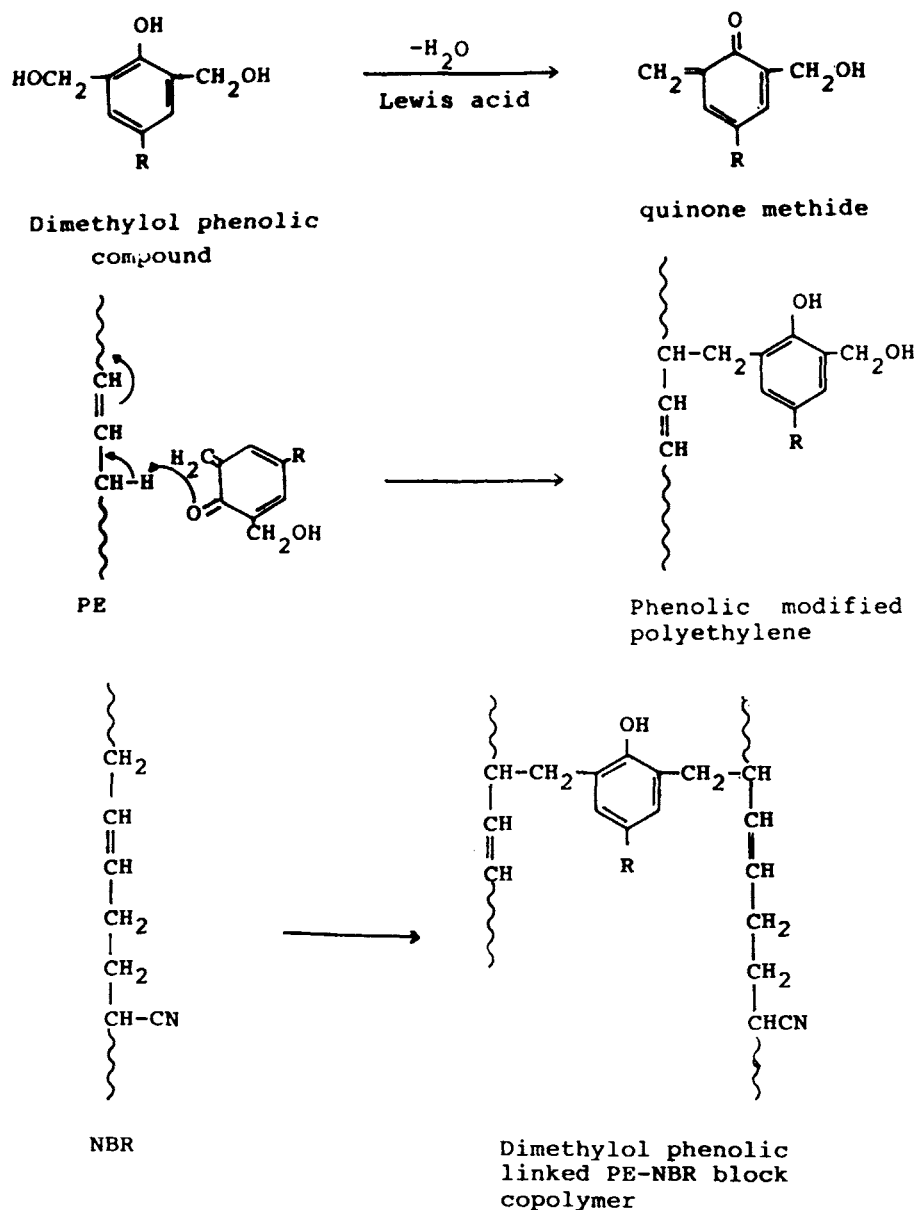
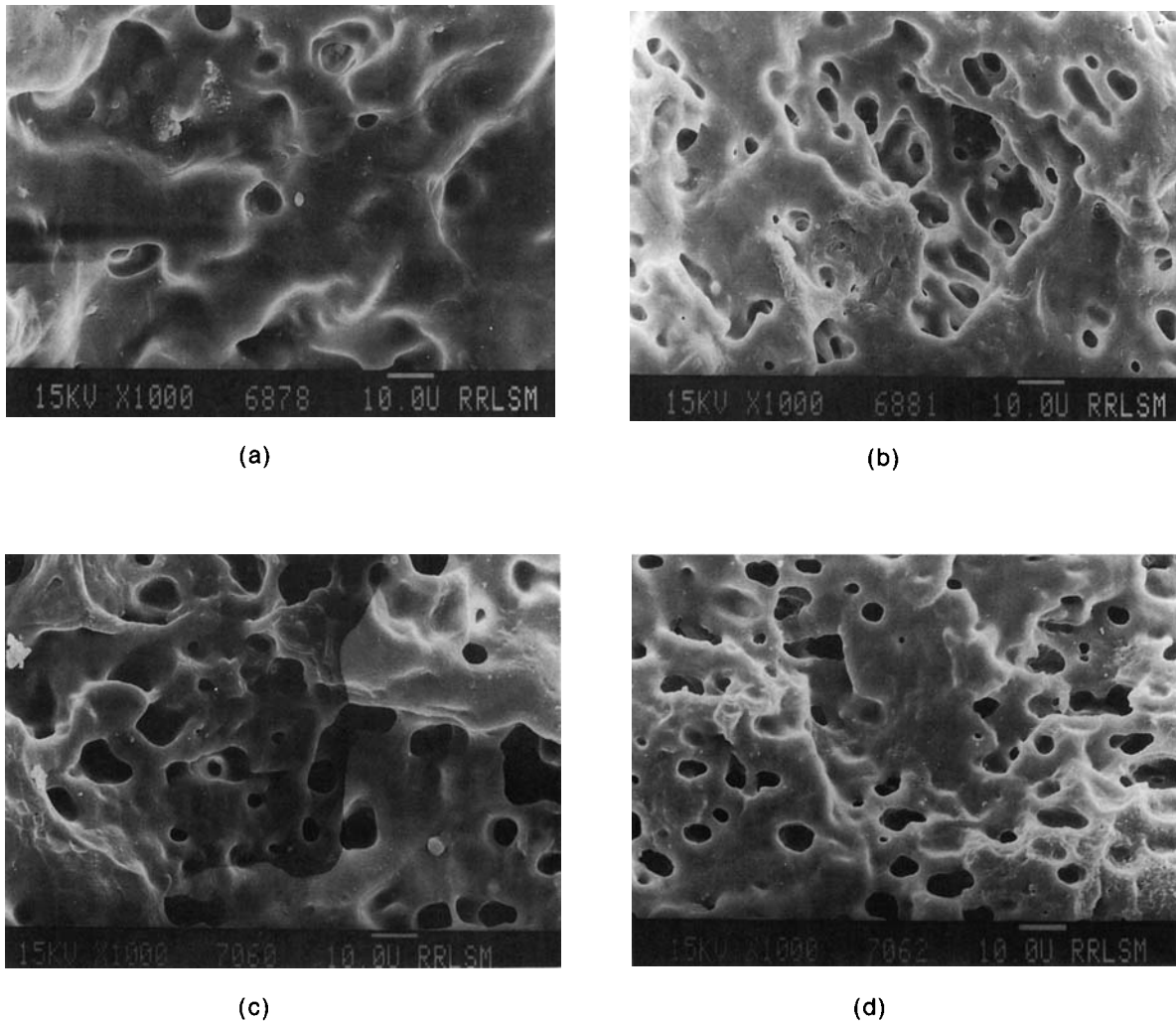


Figure 12 Proposed reaction scheme for phenolic modification on PE.



**Figure 13** SEM photomicrographs of  $H_{70}$  at high magnification to illustrate the state of dispersion at different loadings of MAPE, (a) 1%; (b) 5%; (c) 10%; (d) 15%.

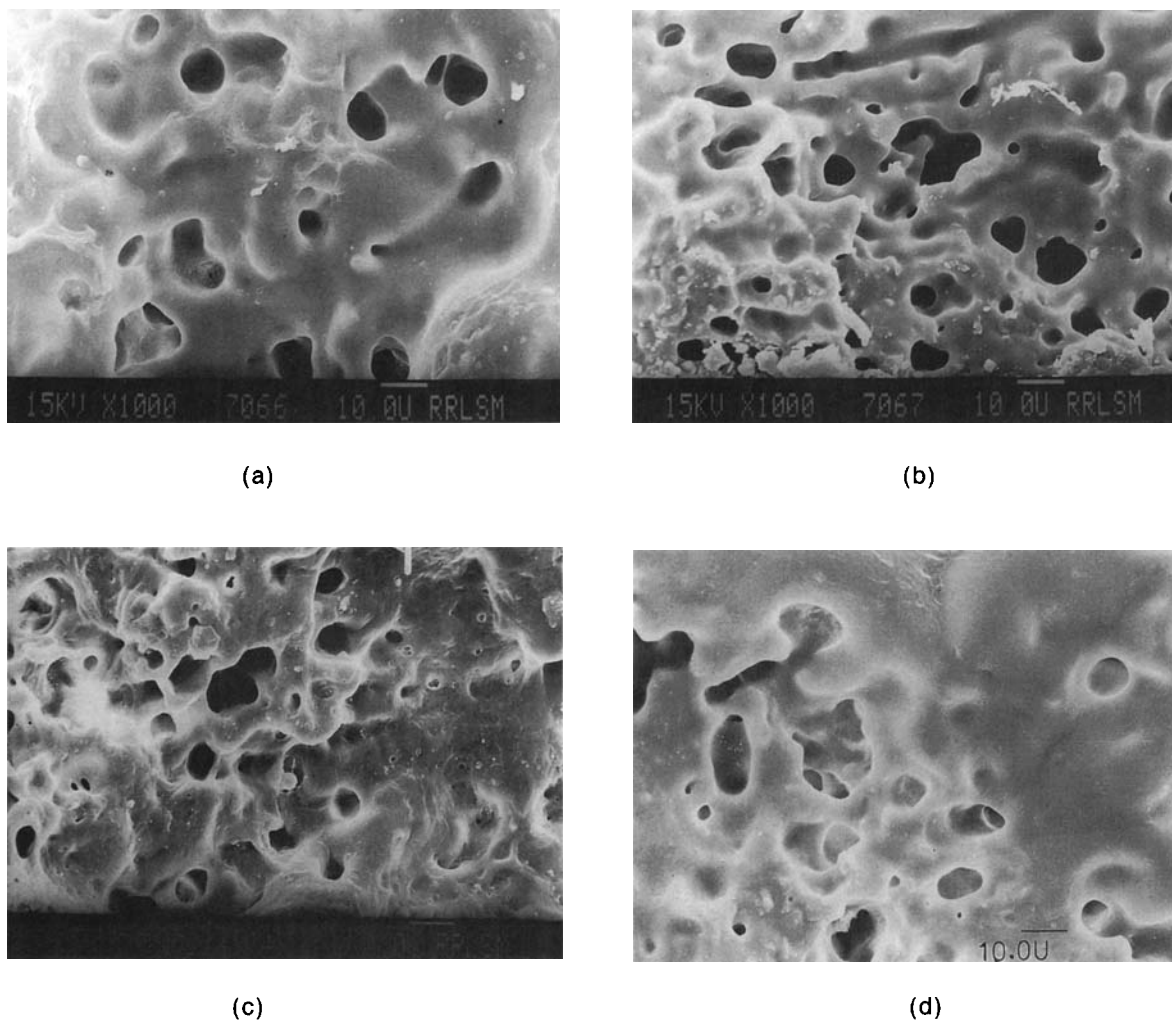
melt mixed with MAN in the presence of DCP. The proposed reaction scheme for phenolic modified polyethylene is shown in Figure 12.<sup>38</sup>

Both MAPE and PhPE act as compatibilizers for HDPE/NBR blends by locating at the interface between the PE matrix and the NBR dispersed phase. The PE chain of the modifier is compatible with the PE matrix, and the polar end is compatible with the NBR phase, thereby enhancing the interfacial adhesion.

#### Effect of Compatibilizers on Morphology and Mechanical Properties

Compatibility between the components is a major determinant of properties of immiscible blends.

There are several reports on the compatibilization of such systems. Riess and co-workers<sup>7,66,67</sup> found that block copolymers are more effective than graft copolymers in increasing the compatibility of PS/PMMA and PS/polyisoprene blends. Gailard and co-workers<sup>68,69</sup> demonstrated the surface activity of block copolymers by studying the interfacial tension reduction in demixed polymer solutions. The interfacial surface activity of copolymer is evident from the sharp reduction in interfacial tension on the addition of small amounts of copolymer. This is followed by a leveling off, which is indicative of interfacial saturation. At higher concentrations micelles of the block copolymer will be formed. The critical micelle concentration (CMC) can be evaluated by

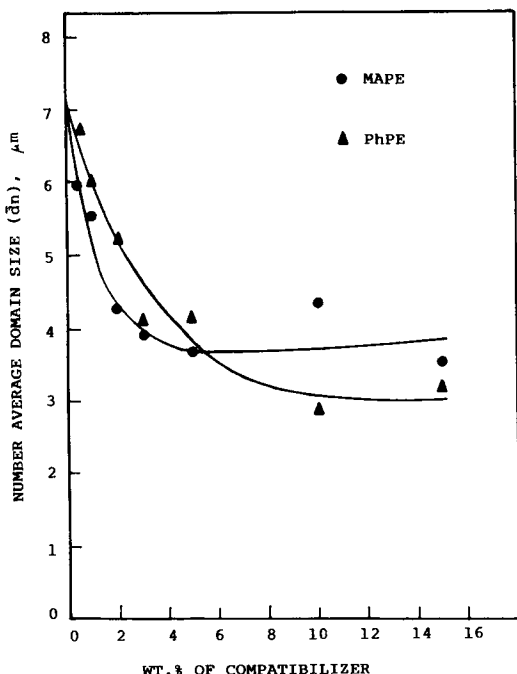


**Figure 14** Scanning electron micrographs illustrating the state of dispersion of  $H_{70}$  at different loadings of PhPE, (a) 1%; (b) 5%; (c) 10%; (d) 15%.

plotting surface tension data vs. copolymer concentration. Nakamura et al.<sup>70</sup> and Riess and co-workers<sup>71,72</sup> reported that the surface tension of a block copolymer solution decreases linearly with increasing concentration below the CMC and reaches an almost constant value when the concentration exceeds CMC. The compatibilization theories of Noolandi and Hong<sup>73</sup> indicate that the reduction in interfacial tension, with increasing copolymer concentration and molecular weight, could be accounted for by the reduction in interaction energy of the block copolymers at the interface, taking into account the associated entropy loss of the localized chains. Anastasiadis et al.<sup>74</sup> have reported on the interfacial tension reduction of PS/1,2 polybutadiene blends by the addition of the corresponding block copolymer.

Thomas and Prud'homme<sup>75</sup> have studied the compatibilizing effect of block copolymers in heterogeneous PS/PMMA blends. Recently, Oommen and Thomas<sup>76</sup> have reported on the interfacial activity of natural rubber-*g*-poly(methyl methacrylate) in incompatible natural rubber/poly(methyl methacrylate) blends.

Figures 13(a) to (d) and 14(a) to (d) show the morphology of  $H_{70}$  upon the addition of MAPE and PhPE as compatibilizers, respectively. The compatibilizer concentrations in (a), (b), (c), and (d) are 1, 5, 10, and 15%, respectively. The number average domain size ( $\bar{d}_n$ ) of the NBR phase has been measured from the photomicrographs. As compared to the uncompatibilized blend [Fig. 6(a)], the dispersed domain size of the compatibilized systems is much smaller. The particle size lies in the range of 7.15



**Figure 15** Effect of compatibilizer concentration on the dispersed phase size of  $H_{70}$ .

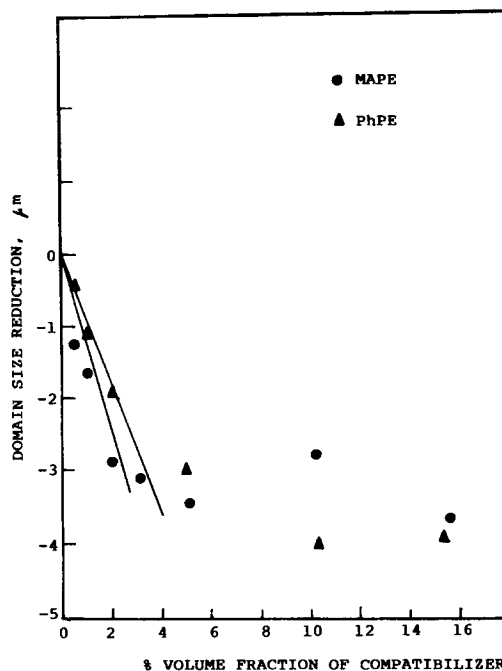
$\mu\text{m}$  for  $H_{70}$ ,  $3.69 \mu\text{m}$  for  $H_{70}M_5$ , and  $2.84 \mu\text{m}$  for  $H_{70}P_{10}$ .

The reduction in particle size as a function of compatibilizer concentration is shown in Figure 15. It is clear from the figure that approximately 5% MAPE is sufficient to produce a maximum reduction of the dispersed phase size. No further reduction in phase size is achieved by adding more compatibilizer, as seen from the plateau region of the plot shown in Figure 15. In the case of PhPE, a higher amount, approximately 8% of compatibilizer, was required for interfacial saturation. The compatibilizers used in the present study, MAPE and PhPE, may form graft or block polymer surfactant molecules *in situ*, which brings about compatibilization. The reaction scheme for the formation of dimethylol phenolic-linked PE-NBR block copolymer is shown in Figure 12. The beginning of the plateau region can be considered as the so-called critical concentration of the compatibilizer, i.e., critical micelle concentration (CMC), required to saturate the interface. Several authors<sup>15-17,74-78</sup> have reported on the equilibration in the phase domain size when increasing amounts of compatibilizer were added to incompatible polymer blend systems. These include the work of Molau et al.,<sup>15-17</sup> Willis and Favis<sup>77</sup> and Teyssie and co-workers,<sup>78</sup> Koberstein and co-workers,<sup>74</sup> Thomas and Prud'homme,<sup>75</sup> and Oommen and Thomas.<sup>76</sup>

Thomas and Prud'homme have reported on the interfacial saturation in heterogeneous PS/PMMA blends upon the addition of PS-*b*-PMMA. The recent study of Oommen and Thomas on the compatibilization of NR/PMMA by NR-*g*-PMMA indicated the equilibration of morphology at higher loadings of the compatibilizer. According to the theories of Noolandi and Hong,<sup>73,79</sup> for concentrations less than the CMC, the interfacial tension is expected to decrease linearly with compatibilizer concentration, whereas above the CMC, a leveling off is expected. All these experimental observations and the theoretical predictions of Noolandi and Hong<sup>73,79</sup> suggest that there is a maximum quantity of compatibilizer that can saturate the interface. Addition of a compatibilizer beyond this point may not modify the interface.

The theories of Noolandi and Hong<sup>73,79</sup> can be applied to highly incompatible systems, such as HDPE/NBR blends for concentrations less than the CMC. According to them,<sup>73,79</sup> in the absence of a solvent, for a ternary system A/A-*b*-B/B, the interfacial tension reduction or increment ( $\Delta\gamma$ ) upon the addition of the copolymer, is given by the following expression.

$$\Delta\gamma = d\phi_c[(1/2\chi + 1/Z_c) - 1/Z_c \exp(Z_c\chi/2)]. \quad (1)$$



**Figure 16** Effect of percent volume fraction of compatibilizers on the domain size reduction of  $H_{70}$ .

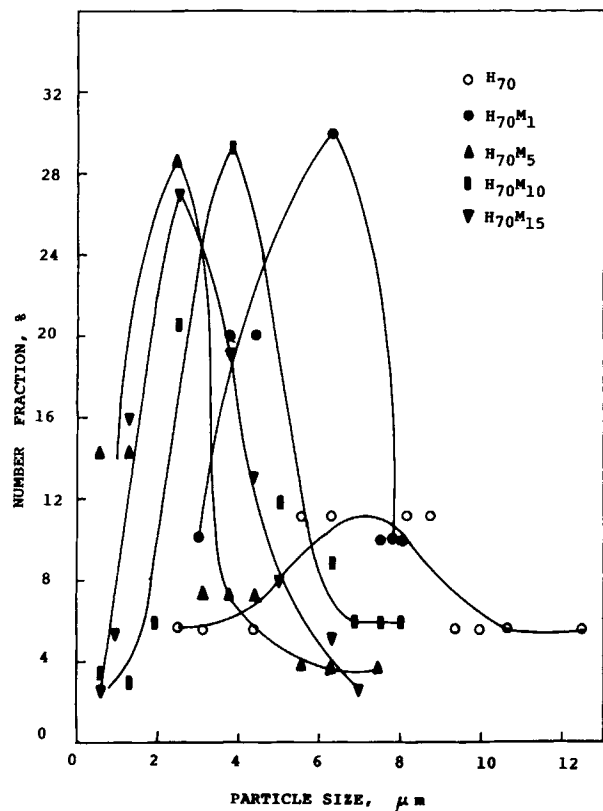


Figure 17 Particle size distribution of H<sub>70</sub> samples containing different loadings of MAPE.

where,  $d$  is the width at half-height of the copolymer profile, reduced by the Kuhn statistical segment length.  $\phi_c$  is the bulk volume fraction of the copolymer in the system,  $\chi$  is the Flory-Huggins interaction parameter between A and B segments of the copolymer, and  $Z_c$  is the degree of polymerization of the copolymer. According to this equation, the plot of interfacial tension reduction vs.  $\phi_c$  should yield a straight line. Although this theory was developed for the action of symmetrical diblock copolymers of A-b-B in incompatible systems (A/B), the theory can be successfully applied to various other systems where the compatibilizing action is not strictly by the addition of symmetrical block copolymers.<sup>80,81</sup> Because the interfacial tension reduction is directly proportional to the particle size reduction,<sup>82</sup> it can be argued that

$$\Delta D = kd\phi_c[(1/2\chi + 1/Z_c) - 1/Z_c \exp(Z_c\chi/2)] \quad (2)$$

where  $\Delta D$  is the particle size reduction or increment upon the addition of the compatibilizer, and  $k$  is a proportionality constant. The plot of exper-

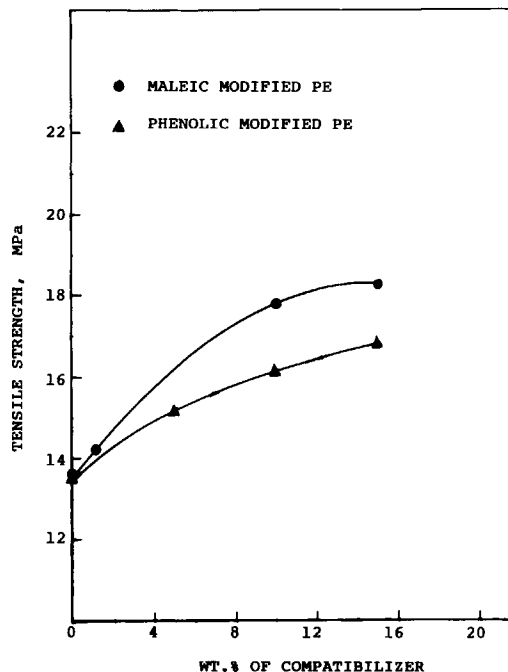


Figure 18 Variation of tensile strength of H<sub>70</sub> as a function of compatibilizer concentration.

imental values of  $\Delta D$  as a function of compatibilizer volume fraction is shown in Figure 16. It can be seen that, at low compatibilizer concentration

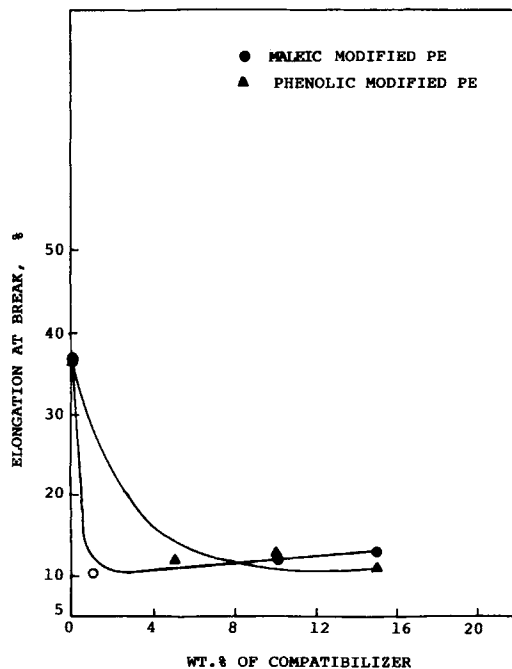


Figure 19 Effect of compatibilizer concentration on the elongation at break of H<sub>70</sub>.

(below the CMC),  $\Delta D$  decreases linearly with increasing compatibilizer volume fraction, whereas, at higher concentrations (above the CMC), it levels off in agreement with the theories of Noolandi and Hong.

The dimensions of the minor phase not only decrease but also attain a more uniform distribution in blends containing a compatibilizer. The work of Willis and Favis<sup>77</sup> clearly demonstrates that for polyolefin/polyamide blends, a broad distribution is obtained for blends without any compatibilizer, but the distribution got significantly narrower when 5% ionomer was added. The particle size distributions became only slightly affected when increased amounts of ionomer were added.

The particle size distributions of uncompatibilized and compatibilized H<sub>70</sub> systems are shown in Figure 17. H<sub>70</sub> shows a broad distribution indicative of incompatibility between HDPE and NBR phases. On the addition of MAPE, the distribution curve has narrowed down. The reduction in particle size and homogeneity in size distribution on the addition of MAPE is due to its ability to reduce the interfacial tension between the dispersed phase and the matrix. Significant narrowing down has occurred up to 5% compatibilizer. The distribution curve is not much affected on further addition of the compatibilizer. These results can be correlated with emulsion studies, where the addition of a surfactant has been shown to narrow down the particle size distribution until a certain concentration of emulsifier is reached.<sup>83</sup>

Addition of a compatibilizer considerably improves the mechanical properties of the blend. The effect of a compatibilizer concentration on the tensile strength and elongation at break of H<sub>70</sub> is shown in Figures 18 and 19, respectively. Uncompatibilized H<sub>70</sub> has much lower tensile strength (13.6 MPa) than the additive value (24.61 MPa). This can be explained by the poor stress transfer between the phases of the immiscible blends, resulting from the large domain size of NBR particles having poor interfacial adhesion, and also by the reduced crystallinity of the blend. By the addition of the compatibilizers, the interfacial condition is improved, and thereby the tensile strength also increases. A leveling off in tensile strength can be observed at 12% compatibilizer concentration in both cases. The tensile strength improvement is more in the case of the MAPE system than for the PhPE system. This may be due to the chances of crosslinking of the HDPE when it is melt mixed with MAN in the presence of DCP. The elongation at break values of the samples,

however, decrease with the addition of compatibilizers.

## CONCLUSION

The tensile strength and modulus data indicate that, within the experimental limits, the best balance of properties can be obtained by blending HDPE and NBR at 180°C for a period of 6 min at 60 rpm. The blend morphology changes with the NBR content. At up to 50% rubber content, NBR exists as the dispersed phase, but at higher rubber contents, cocontinuous morphologies are obtained. From the morphology, it is clear that NBR exists as large domains in the HDPE matrix. The mechanical properties of the uncompatibilized blends show a negative deviation. Maleic-modified polyethylene and phenolic-modified polyethylene were shown to act as compatibilizing agents for HDPE/NBR blends. The high interfacial activity of MAPE reduces the dispersed phase size and provides a more uniform particle size distribution. The dispersed phase size decreases, up to 5% MAPE and 8% PhPE concentrations, followed by a leveling off, which indicates that 5% MAPE or 8% PhPE is sufficient to produce saturation at the interface. For concentrations less than CMC, the theories of Noolandi and Hong predict a linear decrease of interfacial tension with compatibilizer volume fraction. Considering the fact that domain size varies directly with interfacial tension, the experimental data are in agreement with these theories. From the tensile strength and morphological data it is clear that the properties of the blends are substantially improved by the addition of compatibilizers.

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